**REMARKS**

Applicants respectfully request favorable consideration and allowance of the pending claims.

## I. Status of the Claims

Upon entry of this amendment, claims 1-2 and 6-37 remain pending. Claims 7-13, 15-35, and 37 are withdrawn.

Accordingly, the claims under examination at present, which are pending and not withdrawn, include claims 1, 2, 6, 14, and 26. No claims have been amended herein.

## II. Elections/Restrictions

Claim 37 has been marked as withdrawn in view of its dependency on withdrawn claim 35.

## III. Claim Rejections Under 35 U.S.C. §§102(b)/103(a)

Reconsideration is requested of the rejection of claims 1, 2, 6, 14, and 36 as being anticipated by or obvious in view of JP 5-267299, hereinafter "Fujii."

### A. The Claimed Invention

Claim 1 is directed to an alloy for use as a catalyst in oxidation or reduction reactions, the alloy having these three express requirements:

> platinum at a concentration that is between about 10 and about 80 atomic percent;
>
> zinc at a concentration that is between 24 atomic % and about 70 atomic %; and
>
> at least one of nickel and iron at a concentration that is between about 20 atomic % and about 80 atomic %.

Since the alloy defined by claim 1 requires at least about 10 atomic % Pt, at least 24 atomic % Zn, and at least about 20 atomic % of one of Ni or Fe, the sum of the minimum concentrations of Pt, Zn, and Ni/Fe is at least about 54 atomic %. The concentrations of other components, if present at all, may be no greater than about 46 atomic %.

Claim 2 depends from claim 1 and thus requires the concentrations of other components, if present at all, may be no greater than about 46 atomic %. In addition, claim 2 requires the alloy consist essentially of Pt, Zn, and Ni/Fe and thus excludes other components in concentrations that materially affect the basic and novel characteristics of the alloy defined by this claim. See MPEP §2111.03. As defined in applicants' specification at paragraph [0031], an alloy that consists essentially of Pt, Zn, and Ni/Fe is one in which "impurities that do not play a role in the catalytic activity and/or crystallographic structure of the catalyst may be present to some degree". Accordingly, the alloy defined by claim 2 excludes elements that play a role in catalytic activity or affect the crystallographic structure.

Claims 6 are 36 require the sum of the concentrations of Pt, Zn, and Fe/Ni be at least about 59 atomic %. In view thereof, the concentrations of other components, if present at all present, can be no greater than about 41 atomic %.

Claim 14 requires the sum of the concentrations of Pt, Zn, and Fe be at least 89 atomic %. In view thereof, the concentrations of other components, if present at all, can be no greater than about 11 atomic %.

**B. Disclosure of the Fujii Reference**

The Office asserts that the English language abstract of the Fujii reference discloses an alloy comprising:

Pt in a concentration from 0.03 to 37 atomic percent,

Zn in a concentration between 0.1 to 63 atomic percent, and

Fe in a concentration between 0 and 40 atomic percent.

However, this is incorrect. Applicants have obtained a machine assisted translation ("MAT") of the Fujii reference from the Japanese Patent Office website. A MAT may be obtained from the Patent Abstracts of Japan link found at **http://www.ipdl.inpit.go.jp/homepg_e.ipdl**, which is JPO's Industrial Property Digital Library website. A copy of the MAT is attached to this response.

According to the MAT, Fujii discloses a protective copper-based alloy to be applied over copper wiring in a semiconductor integrated circuit device. This is not even remotely relevant to catalysis. In any event, Fujii's protective copper-based alloy may include an alloying element for the purpose of enhancing the corrosion resistance of the alloy. The alloying elements include Ag, Be, Cr, Fe, Mg, Ni, Pd, Si, Sn, Ti, Zn, and Zr in various concentrations. See paragraph [0008] of the MAT. Specific alloys disclosed include copper titanium, copper nickel, copper silver, copper nitride, and copper aluminum [0014]:

> [0014]As a compound of the copper formed, there is a high corrosion resistance alloy like copper-titanium, copper-nickel, and copper-silver or a copper nitride, for example, and if corrosion resistance is maintained, the thinner one as much as possible of the thickness will be good. It is because these compounds have low conductivity compared with copper, so high speed response nature will deteriorate if it becomes thick. Since it is such, as thickness of a copper compound, 0.001-0.1 micrometer is preferred.

Fujii discloses that the addition of an alloying element presents a technical problem of decreased electrical conductivity. See paragraph [0004]: "... electrical

conductivity falls with the increase in the addition of an alloying element. Therefore, it is important technical problem to satisfy the electrical conductivity as a wiring material, ..."

Since maintenance of electrical conductivity is important to the function of the protective copper-based film as a wiring material, the ordinarily skilled person would understand this disclosure as teaching that the concentration of alloying elements should be sufficient to achieve enhanced corrosion protection, but also should be minimized so as not to unduly impair electrical conductivity. In electronic devices, such as integrated circuits, conductivity is critical. Copper is second only to silver in electrical conductivity, so alloying copper with elements such as Pt, Zn, Ni, or Fe necessarily decreases electrical conductivity of the alloy, and concentrations of these elements that are too high would impair the ability of the alloy to function as a wiring material. The ordinarily skilled person would thus understand that the concentration disclosures in Fujii may be sufficient to enhance corrosion protection, but would also understand that the concentrations should be minimized to avoid deleterious reduction in conductivity.

Claim 1 is neither anticipated nor rendered obvious by Fujii since the cited reference does not disclose or fairly suggest any catalyst material having all of the components and component concentrations required by claim 1. If anything, Fujii materially teach away from the alloy defined by claim 1.

**C. Anticipation**

With regard to anticipation, MPEP §2131 requires:

"A claim is anticipated only if each and every element as set forth in the claim is found, either expressly or inherently described, in a single prior art

> reference." *Verdegaal Bros. v. Union Oil Co. of California*, 814 F.2d 628, 631, 2 USPQ2d 1051, 1053 (Fed. Cir. 1987). >"When a claim covers several structures or compositions, either generically or as alternatives, the claim is deemed anticipated if any of the structures or compositions within the scope of the claim is known in the prior art." *Brown v. 3M*, 265 F.3d 1349, 1351, 60 USPQ2d 1375, 1376 (Fed. Cir. 2001) (claim to a system for setting a computer clock to an offset time to address the Year 2000 (Y2K) problem, applicable to records with year date data in "at least one of two-digit, three-digit, or four-digit" representations, was held anticipated by a system that offsets year dates in only two-digit formats). See also MPEP § 2131.02.< ***"The identical invention must be shown in as complete detail as is contained in the ... claim."*** *Richardson v. Suzuki Motor Co.*, 868 F.2d 1226, 1236, 9 USPQ2d 1913, 1920 (Fed. Cir. 1989). ***The elements must be arranged as required by the claim,*** but this is not an *ipsissimis verbis* test, i.e., identity of terminology is not required. *In re Bond*, 910 F.2d 831, 15 USPQ2d 1566 (Fed. Cir. 1990).

Under *Richardson*, the "complete detail" required for the Fujii disclosure to anticipate the claims requires a showing that Fujii disclose an alloy comprising Pt, Zn, and at least one of Fe or Ni, and each element is present at a concentration within the claimed concentration ranges. The only alloys disclosed in Fujii are copper titanium, copper nickel, copper silver, copper nitride, and copper aluminum, so Fujii does not disclose any alloy having the components required by the claims, much less any alloy in which the component concentrations are within the concentration ranges required by the claims. Accordingly, Fujii's disclosure does not anticipate the claims.

If anticipation is to be based on Fujii's disclosure of several elements that may be alloyed with copper, including Ag, Be, Cr, Fe, Mg, Ni, Pd, Pt, Si, Sn, Ti, Zn, and Zr, the Office

must show that the species of the claims is "at once envisaged" by the broad, generic disclosure. MPEP § **2131.02** requires:

> **A GENERIC CHEMICAL FORMULA WILL ANTICIPATE A CLAIMED SPECIES COVERED BY THE FORMULA WHEN THE SPECIES CAN BE "AT ONCE ENVISAGED" FROM THE FORMULA**
>
> When the compound is not specifically named, but instead it is necessary to select portions of teachings within a reference and combine them, e.g., select various substituents from a list of alternatives given for placement at specific sites on a generic chemical formula to arrive at a specific composition, anticipation can only be found if the classes of substituents are sufficiently limited or well delineated. *Ex parte A*, 17 USPQ2d 1716 (Bd. Pat. App. & Inter. 1990). If one of ordinary skill in the art is able to "at once envisage" the specific compound within the generic chemical formula, the compound is anticipated. One of ordinary skill in the art must be able to draw the structural formula or write the name of each of the compounds included in the generic formula before any of the compounds can be "at once envisaged." One may look to the preferred embodiments to determine which compounds can be anticipated. *In re Petering*, 301 F.2d 676, 133 USPQ 275 (CCPA 1962).
>
> Compare *In re Meyer,* 599 F.2d 1026, 202 USPQ 175 (CCPA 1979) (A reference disclosing "alkaline chlorine or bromine solution" embraces a large number of species and cannot be said to anticipate claims to "alkali metal hypochlorite."); *Akzo N.V. v. International Trade Comm'n*, 808 F.2d 1471, 1 USPQ2d 1241 (Fed. Cir. 1986) (Claims to a process for making aramid fibers using a 98% solution of sulfuric acid were not anticipated by a reference which disclosed using sulfuric acid solution but which did not disclose using a 98% concentrated sulfuric acid solution.). See **MPEP § 2144.08** for a discussion of obviousness in genus-species situations.

The proper analysis requires consideration of whether a reference disclosing a copper-based protective coating that may be alloyed with any of Ag, Be, Cr, Fe, Mg, Ni, Pd, Pt, Si, Sn,

Ti, Zn, and Zr allows one to "at once envisage" the specific claimed alloy comprising Pt, Zn, and at least one of Fe or Ni. In this regard, the possible number of binary, ternary, quaternary and other alloys possible from this list is very large. There are 13 different binary alloys comprising Cu (which is a required element in Fujii's Cu-based alloy) and at least one of the alloying elements, 78 ternary alloys comprising Cu and at least two of the alloying elements, 286 quaternary alloys comprising Cu and at least three of the alloying elements, and 715 quinary alloys comprising Cu and at least four of the alloying elements, and even greater number of senary, septenary, etc. alloys. In order to anticipate the claims, the ordinarily skilled person would have had to "at once envisage" the alloys comprising Cu, Pt, Zn, and at least one of Fe or Ni out of this large number of possible combinations and permutations. *Meyer's* holding, as endorsed by the MPEP, precludes anticipation since disclosure embracing "a large number of species ... cannot be said to anticipate claims ..."

Applicants' claims are not, however, merely directed to alloys comprising Pt, Zn, and at least one of Fe or Ni generically. Rather, the claims additionally delineate concentration ranges for each element in the alloy. Accordingly, not only would the ordinarily skilled person have to "at once envisage" an alloy comprising Pt, Zn, and Fe/Ni to anticipate the claims, Fujii's disclosure would also have to disclose concentrations within the claimed range. Fujii's disclosure does not anticipate the claims since Fujii does not disclose any alloy in which component concentrations are within the required concentration ranges. In Fujii's alloy, copper is a major element, perhaps the predominant element in the alloy, since Fujii's invention is directed to copper-based alloys useful as protective coatings over copper wires and thus must be

a "wiring material." See [0004] of the MAT. In this respect, high electrical conductivity is required. Accordingly, copper must be present in a sufficiently high concentration in order for the copper alloy protective layer to function effectively as a corrosion resistant film that does not impair the necessary electrical conductivity properties of the underlying copper wire. See paragraph [0004] of the MAT, which discloses that "... electrical conductivity falls with the increase in the addition of an alloying element... " See also paragraph [0020], which discloses an alloy in which the copper concentration was 60%. Importantly, this alloy further contained aluminum, which is also a highly electrically conductive metal. Pt, Zn, Fe, and Ni are much less electrically conductive than copper. See, e.g., **http://environmentalchemistry.com/yogi/periodic/electrical.html**, which shows that Pt and Fe have about 16% of copper's conductivity and Zn and Ni have about 25% of copper's conductivity. Fujii's disclosure, especially paragraph [0004], thus clearly establishes that alloying elements -- like those in claim 1 -- should be present only in concentrations sufficient to achieve corrosion protection, but must not be so high as to impair the electrical conductivity of the protective coating.

The alloy defined by claim 1 requires the concentrations of the Pt, Zn, and at least one of Fe and Ni sum to at least about 54 atomic %. Fujii does not disclose any alloy comprising Cu-Pt-Zn-Fe/Ni in which the copper content is less than 46 atomic % and the other components are present within the claimed concentration ranges. Such an alloy is not within the purview of Fujii's disclosure since Fujii discloses that high concentrations of Pt, Zn, and Fe or Ni would necessarily lower the electrical conductivity of the alloy, which Fujii explicitly disclosed is a result to be avoided.

The alloy concentration ranges disclosed in Fujii at paragraph [0008], such as 0.1 to 50 wt.% Pt, 0.1 to 50 wt.% Zn, 0.3 to 20 wt.% Fe, and 0.2 to 50 wt.% Ni, thus must be read with the understanding that Fujii's alloy is based on copper, as disclosed in the Abstract and elsewhere. Accordingly, recitation of a range of Pt from 0.1 to 50 wt.% means that if the Pt content can be as high as 50 wt.%, the alloy is a binary alloy with Cu and Pt and the copper content is 50 wt.% or more. If other elements are added that may adversely affect conductivity, Cu must remain a major element to maintain acceptable electrical conductivity. Accordingly, the concentrations of all of the other elements must be less than 50 wt.%, and likely substantially less than 50 wt.%.

Since no alloy having all of the components required in the claims is disclosed in Fujii and since Fujii do not disclose any alloy in which the component concentrations are within the claimed ranges, Fujii's disclosure does not anticipate claim 1 or any of its dependent claims.

Claim 2 requires the alloy consist essentially of platinum, zinc, and at least one of nickel and iron. Fujii's disclosure does not anticipate claim 2 since Fujii's alloy is copper-based and the copper concentration must be high in order to maintain electrical conductivity. Since copper is a major, if not the predominant, element in Fujii's alloy, copper would necessarily affect at least one of the "catalytic activity and/or crystallographic structure of the catalyst." Such elements are excluded from the alloy defined by claim 2. See paragraph [0031] of applicants' specification. In view thereof, Fujii's copper requirement materially affects the basic characteristics of the alloy.

**D. Obviousness**

The comments above with respect to anticipation additionally pertain to obviousness. *Prima facie* obviousness is not established herein since Fujii does not disclose or suggest any alloy comprising Pt, Zn, and Fe/Ni in which the components have concentrations within the claimed concentration ranges. See MPEP §2143.03, which states that "All Claim Limitations Must be *Considered*." Additionally, *CFMT, Inc. v. Yieldup International Corp.*, 349 F.3d 1333, 1342 (Fed. Cir. 2003) establishes that "obviousness requires a suggestion of all limitations in a claim," citing *In re Royka*, 490 F.2d 981, 985 (CCPA 1974). See also *Ex Parte Alan Gerwitz*, Appeal 2009-006223 (February 24, 2010), 2010 WL 676170 at *9 (BPAI). A proper obviousness determination requires that the Office make "a searching comparison of the claimed invention - *including all its limitations* - with the teaching of the prior art." *See In re Wada and Murphy*, Appeal 2007-3733 (January 14, 2008), *citing In re Ochiai*, 71 F.3d 1565, 1572 (Fed. Cir. 1995) (emphasis in original). Further, the Supreme Court held that obviousness is a question of law based on underlying factual inquiries, including ... ascertaining the differences between *the claimed invention* and the prior art. *Graham v. John Deere Co.*, 383 U.S. 1, 148 USPQ 459 (1966) (emphasis added). MPEP §904 instructs examiners that "The first search should cover the invention as described and claimed, including the inventive concepts toward which the claims appear to be directed."

In sum, it remains well-settled law that obviousness requires at least a suggestion of all of the features in a claim. *See In re Wada and Murphy*, *citing CFMT, Inc. v. Yieldup Intern. Corp.*, 349 F.3d 1333, 1342 (Fed. Cir. 2003) and *In re Royka*, 490 F.2d 981, 985 (CCPA 1974)). Again, Fujii discloses a copper-based alloy used to protect copper wiring in a semiconductor integrated circuit device. In the Abstract, the

alloy is referred to as a "copper compound" and "[t]he alloy is made of copper..." Copper is thus the basic component of the alloy, as evidenced by the disclosure that maintaining high conductivity is important and the disclosure of certain alloys that contain, e.g., 60% copper with aluminum, and by the reference in [0014] to *only* "copper-titanium, copper-nickel, and copper-silver or a copper nitride."

Fujii also teach away from the alloys defined by the claims. Although the alloy contains additional elements added to enhance corrosion protection, as stated in paragraph [0004] of the MAT, "electrical conductivity falls with the increase in the addition of an alloying element." This is a material teaching away from any alloy which comprises a substantial quantity of any element other than copper. See MPEP §2141.02 Part V.:

> **VI. PRIOR ART MUST BE CONSIDERED IN ITS ENTIRETY, INCLUDING DISCLOSURES THAT TEACH AWAY FROM THE CLAIMS**
> A prior art reference must be considered in its entirety, i.e., as a whole, including portions that would lead away from the claimed invention. *W.L. Gore & Associates, Inc. v. Garlock, Inc.*, 721 F.2d 1540, 220 USPQ 303 (Fed. Cir. 1983), *cert. denied*, 469 U.S. 851 (1984)

Fujii's disclosure is a material teaching away from the claimed invention since they disclose that the copper-based alloy is intended for use as a protective covering over a copper wire in a semiconductor integrated circuit device. Electrical conductivity of the copper wire is a critical consideration in the manufacture of IC devices, so any coating layer that may impair electrical conductivity is undesirable and must be avoided. Fujii's disclosure that alloying elements decrease the electrical conductivity materially teaches away from any concentration of alloying elements beyond a minimum needed to

achieve the required corrosion enhancement. In view thereof, Fujii's alloys, e.g., the 60% Cu-40% Al alloy, contain substantially more copper than alloying elements. The ordinarily skilled person would not have found any reason whatsoever to have modified Fujii's elements in order to prepare an alloy having the requirements of claim 1, which defines an alloy comprising at least 54 atomic % Pt, Zn, and at least one of Fe or Ni since such an alloy would have substantially less electrical conductivity than an alloy having more than 50 atomic % copper.

In view of the foregoing, claim 1 is non-obvious over Fujii, and applicants' respectfully request the rejection be withdrawn.

Fujii teach away from the alloys of the dependent claims, which consist essentially of platinum, zinc, and at least one of nickel and iron as required by claim 2 or contain even higher concentrations of Pt, Zn, and Fe/Ni in the alloy as required by claims 6, 14, and 36.

**CONCLUSION**

In view of the foregoing, applicants request issuance of a Notice of Allowance for all pending claims.

Applicants do not believe that a fee is required for the filing of this response, as it is being submitted within the three month shortened statutory period for reply. Should applicants be incorrect, the Commissioner is hereby authorized to charge the necessary fee to Deposit Account No. 19-1345.

Respectfully submitted,

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# PATENT ABSTRACTS OF JAPAN

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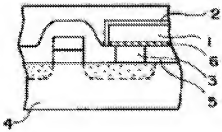
KOBAYASHI SHIRO

## (54) SEMICONDUCTOR DEVICE

(57)Abstract:

PURPOSE: To obtain a semiconductor device excelling in its high-speed response quality and in its reliability while using a wiring material excelling in its electric conductivity, thermal resistance, quality resistant to electromigration, oxidation resistance, and corrosion resistance, by so providing a copper comound having the higher corrosion resistance than copper as to cover the surfaces of a circuit wiring made of copper or a copper alloy, etc.




CONSTITUTION: In the semiconductor chip of a semiconductor device, the materials of a circuit wiring 1 and/ or an electrode are equally copper or a copper compound. A copper compound 2 has such a high corrosion resistance that its relative oxidation quantity is not more than 50% of the one of copper. In this semiconductor device, the copper compound 2 is so provided as to cover the surface of the circuit wiring 1. As the copper compound 2, the following alloy or the following compound is preferred. The alloy is made of copper

and at least one kind of metallic element selected from Ag, Be, Cr, Fe, Mg, Ni, Pd, Pt, Si, Sn, Ti, Zn, and Zr. The compound is made of copper and one of non-metalic elements of N and P.

For example, the surface of a copper wiring 1, which is formed on a metallic film 5 for an ohmic contact via a barrier metal 6, is covered with a copper-nickel alloy 2 having a high corrosion resistance.

JAPANESE [JP,05-267299,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]



## CLAIMS

[Claim(s)]
[Claim 1]A semiconductor device, wherein a compound of copper in which relative oxidation quantity has 50% or less of high corrosion resistance from copper is -ed **(ed) by the surface in a semiconductor device whose circuit wiring in a semiconductor chip and/or material of an electrode are copper or a copper alloy.
[Claim 2]In a semiconductor device whose circuit wiring in a semiconductor chip and/or material of an electrode are copper or a copper alloy, Copper, Ag, Be, Cr, Fe and Mg, nickel, Pd, Pt, Si, Sn, Ti, Zn, a semiconductor device, wherein an alloy with at least one or more kinds of metallic elements of Zr is -ed **(ed) by the surface.
[Claim 3]In the semiconductor device according to claim 2, content of a metallic element uses weight %, Ag;. 0.2 to 50%, Be;. 0.05 to 10%, Cr;. 0.05 to 50%, Fe;. 0.03 to 20%, Mg;0.5-20%, nickel;0.2-50%, Pd;0.1-50%, Pt;0.1-50%, Si;0.04-10%, Sn;0.1-50%, Ti;0.5-50%, Zn;0.1-50%, Zr; that it is 0.01 to 50%. A semiconductor device by which it is characterized.
[Claim 4]A semiconductor device, wherein a compound

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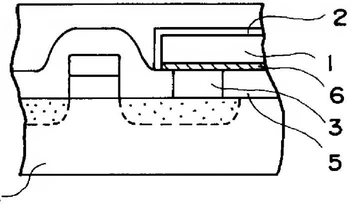


1 銅配線
2 Cu−Ni合金

[Translation done.]

with a nonmetallic element of copper, N, or P is -ed **(ed) by the surface in a semiconductor device whose circuit wiring in a semiconductor chip and/or material of an electrode are copper or a copper alloy.
[Claim 5]A semiconductor device which content of a nonmetallic element uses weight % in the semiconductor device according to claim 4, and is characterized by being N; 0.005 to 10%, and P; 0.01 to 10%.
[Claim 6]A metal membrane for ohmic contacts with semiconductor membrane, copper, or a copper alloy, and a metal barrier to copper or a copper alloy, A process of forming copper or a copper alloy in piles one by one, and a process which describes a circuit by a photoresist on said each film, and carries out dry etching according to the depiction pattern, A process of forming a compound of copper which has corrosion resistance higher than the copper or copper alloy selectively on copper exposed after dry etching, or the copper alloy surface, Circuit wiring in a semiconductor chip having the process of forming a compound of copper which has corrosion resistance higher than the copper or copper alloy selectively on a process of removing a photoresist, copper exposed after photoresist removal, or the copper alloy surface, and/or a formation method of an electrode.
[Claim 7]A metal membrane for ohmic contacts with semiconductor membrane, copper, or a copper alloy, and a metal barrier to copper or a copper alloy, A process of forming copper or a copper alloy in piles one by one, and a process of carrying out pattern NINGU of said each film, and forming a circuit pattern, Circuit wiring in a semiconductor chip having a process of forming a compound of copper which has corrosion resistance higher than the copper or copper alloy, and the process of carrying out pattern NINGU of the compound of the copper, and forming a circuit pattern, and/or a formation method of an electrode.
[Claim 8]A metal membrane for ohmic contacts with semiconductor membrane, copper, or a copper alloy, and copper or a metal barrier of a copper alloy, A process of forming copper or a copper alloy in piles one by one, and a process of carrying out pattern NINGU of said each film, and forming a circuit pattern, Circuit wiring in a semiconductor chip having the process of forming a compound of copper which has corrosion resistance higher than the copper or copper alloy selectively on copper or the copper alloy surface, and/or a formation method of an electrode.

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[Translation done.]

JAPANESE [JP,05-267299,A]

CLAIMS DETAILED DESCRIPTION TECHNICAL FIELD PRIOR ART EFFECT OF THE INVENTION TECHNICAL PROBLEM MEANS OPERATION EXAMPLE DESCRIPTION OF DRAWINGS DRAWINGS

[Translation done.]

* NOTICES *



## DETAILED DESCRIPTION

[Detailed Description of the Invention]
[0001]
[Industrial Application]This invention relates to semiconductor device copper whose circuit wiring in a semiconductor chip and/or material of an electrode are copper or a copper alloy and its electrode, or the formation method of wiring.
[0002]
[Description of the Prior Art]Conventionally, the aluminum alloy has been used for the circuit wiring and the electrode material of a semiconductor device. In recent years, with high integration of a semiconductor device, the minuteness making of a circuit pattern advances and 0.5 micrometer or less has been required as wiring width. However, we are anxious about problems, such as a fall of the circuit speed of response by the increase in wiring delay time, and a fall of the wiring life by advance of the electromigration by the increase in calorific value, or the increase in current density, with reduction of a wiring cross-section area. In order to avoid this problem, like a description to JP,S61-294838,A, JP,H63-248538,A, or JP,S62-290150,A, The wiring material using copper or the copper alloy which excelled the aluminum system wiring material in electrical conductivity, heat resistance, and electromigration-proof nature is developed. That is, compared with aluminum, 2/3 and the melting point of electrical resistance are high not less than 400 **,

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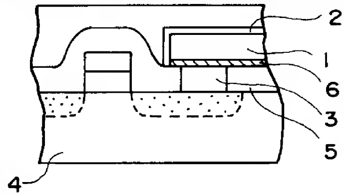


1 銅配線
2 Cu—Ni合金

[Translation done.]

and since copper is excellent also in the wiring life by advance of electromigration 10 or more times, when a semiconductor device is formed, it can aim at the high speed response nature and improvement in reliability.

[0003]

[Problem(s) to be Solved by the Invention]However, copper has a problem in respect of electrical conductivity with a copper alloy in respect of oxidation resistance and corrosion resistance. That is, since the protection nature of copper of the oxide film generated on the surface is low compared with aluminum, it is easy to receive high temperature oxidation, and easy to corrode in an acidic solution. Since a wiring material is put to oxidizing solution environment like high temperature gas atmosphere or a ** fluoric acid solution in the manufacturing process or body ******** is examined in the inspection process after an assembly, high corrosion resistance is required.

[0004]In the copper alloy which aimed at oxidation-resistant and corrosion-resistant improvement, there is a problem that electrical conductivity falls with the increase in the addition of an alloying element. Therefore, it is important technical problem to satisfy the electrical conductivity as a wiring material, heat resistance, and electromigration-proof nature, and to aim at improvement in further oxidation resistance and corrosion resistance.

[0005]The purpose of this invention is to provide the formation method of the semiconductor device excellent in high speed response nature and reliability and its wiring, or an electrode by using the wiring material excellent in electrical conductivity, heat resistance, electromigration-proof nature, and oxidation resistance and corrosion resistance.

[0006]

[Means for Solving the Problem]The above-mentioned purpose is attained by semiconductor device using a wiring material in which a copper alloy or an intermetallic compound excellent in conductivity and oxidation resistance, or corrosion resistance was formed on the copper surface.

[0007]Namely, as for this invention, a compound of copper in which relative oxidation quantity has 50% or less of high corrosion resistance from copper in a semiconductor device whose circuit wiring in a semiconductor chip and/or material of an electrode are copper or a copper alloy was -ed **(ed) by the surface.

[0008]In a semiconductor device whose circuit wiring in a semiconductor chip and/or material of an electrode of this invention are copper or a copper alloy, An alloy with at least one or more kinds of metallic elements of copper, Ag, Be, Cr, Fe and Mg, nickel, Pd, Pt, Si, Sn, Ti, Zn, and Zr was -ed **(ed) by the surface. Content of a metallic element uses weight % here, Ag;. 0.2 to 50%, Be;. 0.05 to 10%, Cr;. 0.05 to 50%, Fe;. 0.03 to 20%, Mg;0.5-20%, nickel;0.2-50%, Pd:0.1-50%, Pt;0.1-50%, Si;0.04-10%, Sn;0.1-50%, Ti;0.5-50%, Zn;0.1-50%, Zr; what is 0.01 to 50% is good.

[0009]As for this invention, in a semiconductor device whose circuit wiring in a semiconductor chip and/or material of an electrode are copper or a copper alloy, a compound with a nonmetallic element of copper, N, or P was -ed **(ed) by the surface. Here, content of a nonmetallic element uses weight % and what is N; 0.005 to 10% and P; 0.01 to 10% is good.

[0010]A process of forming a copper compound this invention is characterized by that comprises the following, Circuit wiring in a semiconductor chip having the process of forming a compound of copper which has corrosion resistance higher than the copper or copper alloy selectively on a process of removing

a photoresist, copper exposed after photoresist removal, or the copper alloy surface, and/or a formation method of an electrode.
Semiconductor membrane, copper, or a metal membrane for ohmic contacts with a copper alloy.
A metal barrier to copper or a copper alloy.
A process of forming copper or a copper alloy in piles one by one.
It is corrosion resistance higher than the copper or copper alloy selectively on a process which describes a circuit by a photoresist on said each film, and carries out dry etching according to the depiction pattern, copper exposed after dry etching, or the copper alloy surface.

[0011]Circuit wiring in a semiconductor chip, wherein this invention has a process of forming a copper compound characterized by comprising the following, and the process of carrying out pattern NINGU of the compound of the copper, and forming a circuit pattern and/or a formation method of an electrode.
Semiconductor membrane, copper, or a metal membrane for ohmic contacts with a copper alloy.
A metal barrier to copper or a copper alloy.
A process of forming copper or a copper alloy in piles one by one.
A process of carrying out pattern NINGU of said each film, and forming a circuit pattern, and corrosion resistance higher than the copper or copper alloy.

[0012]Circuit wiring in a semiconductor chip, wherein this invention has the process of forming a copper compound characterized by comprising the following and/or a formation method of an electrode.
Semiconductor membrane, copper, or a metal membrane for ohmic contacts with a copper alloy.
Copper or a metal barrier of a copper alloy.
A process of forming copper or a copper alloy in piles one by one.
It is corrosion resistance higher than the copper or copper alloy selectively on a process of carrying out pattern NINGU of said each film, and forming a circuit pattern, and copper or the copper alloy surface.

[0013]
[Function]By forming the compound of copper excellent in oxidation resistance or corrosion resistance on the copper interconnect surface excellent in electrical conductivity, heat resistance, and electromigration-proof nature according to this invention, The wiring material which has the electrical conductivity which copper has, heat resistance, electromigration-proof nature and the oxidation resistance which a copper compound has, and corrosion resistance is obtained.
[0014]As a compound of the copper formed, there is a high corrosion resistance alloy like copper-titanium, copper-nickel, and copper-silver or a copper nitride, for example, and if corrosion resistance is maintained, the thinner one as much as possible of the thickness will be good. It is because these compounds have low conductivity compared with copper, so high speed response nature will deteriorate if it becomes thick. Since it is such, as thickness of a copper compound, 0.001-0.1 micrometer is preferred.
[0015]The addition of an alloying element is specified from it being prescribed by the mechanical property and making it that the alloy of the maximum is electric, and, as for the minimum, oxidation depressor effect show up. Then, the addition of each element has the following good ranges. Content of a metallic element is made into weight %, Ag;. 0.2 to 50%, Be;. 0.05 to 10%, Cr;. 0.05 to 50%, Fe;. 0.03 to 20%, Mg;0.5-

20%, nickel;0.2-50%, Pd:0.1-50%, Pt;0.1-50%, Si;0.04-10%, Sn;0.1-50%, Ti;0.5-50%, Zn;0.1-50%, Zr; it is 0.01 to 50%. Content of a nonmetallic element is made into weight %, and is N; 0.005 to 10%, and P; 0.01 to 10%.
[0016]Cu-metallic element alloy controls oxidation by the protective action of the oxide film generated on the surface. That is, the surface of metal is covered with the oxide of only a minimum quantity required to control oxidation. On the other hand, itself of Cu-N and Cu-P which were generated on the surface is a stable compound to oxidation.
Since oxygen and metal are isolated with this compound, metaled oxidation does not advance.

[0017]A copper compound is formed by physical or chemical methods, such as a vacuum deposition method, a sputtering technique, the ion plating method, the ion cluster beam method, a plasma reaction method, and chemical vapor deposition.
[0018]
[Example]The sectional view of the semiconductor device which gave this invention is shown in drawing 1. Since the surface of the copper interconnect 1 is covered with the corrosion-resistant high copper-nickel alloy 2, the corrosion of the copper interconnect 1 is controlled also in a subsequent process by this invention. In a figure, a metal layer for 3 to take a silica dioxide, for 4 take a silicon wafer, and for 5 take ohmic contact and 6 show a metal barrier. Drawing 2 is the figure which plotted the relative oxidation quantity of the copper interconnect to the nickel concentration at the time of adding nickel to Cu. Drawing 2 shows that oxidation depressor effect shows up, when 0.2% of the weight or more of nickel is added.
Since the formed copper-nickel alloy 2 is very thin, an electrical property or its thermal characteristic is equivalent to the characteristic of the copper interconnect 1. It excels in anticorrosion reliability by this invention, and the semiconductor device which has the same electrical conductivity as copper, heat resistance, and electromigration-proof nature can be provided.
[0019]The result of the oxidation test by the oxygen plasma of various kinds of copper interconnects which gave this invention is shown in drawing 3. The copper interconnect which gave this invention is put into fixed time oxygen plasma, and is oxidized. Oxidation quantity turned the quantity of the copper oxide after an examination in fixed quantity with the electrochemical process. Compared with the oxidation quantity of the copper interconnect (Cu) which does not process this invention, silver, iron, nickel, It turns out that the direction of the copper interconnect (Cu-1Ag, Cu-1Fe, Cu-1nickel, Cu-1Zn, Cu-1Zr) in which zinc or a zirconium alloy was formed, or the copper interconnect (Cu-N) in which nitriding copper was formed is decreasing to 50% or less. It became clear that the copper interconnect which gave this invention has high oxidation resistance compared with the conventional copper interconnect from this.
[0020]Although the relative oxidation quantity of the Cu-1 aluminum alloy (JP,S62-290150,A) was shown in drawing 3, it turns out that it cannot be said that this figure to Cu-1 aluminum alloy is about 60% of Cu, is over 50%, and is enough as oxidation depressor effect. There are two techniques in oxidation-resistant improvement by alloying. ** Add the metal which cannot oxidize easily, such as the precious metals, (Ag). ** Add the metal which oxidizes easily, make the oxide film of protection nature form in the surface, and protect an alloy (nickel etc.). Compatibility of aluminum with oxygen is higher than Cu, and the oxidation depressor effect of the oxide itself is still higher. However, it seems that sufficient oxidation depressor

effect is not acquired since the movement speed of aluminum in a Cu alloy is small and aluminum of sufficient quantity for the oxide of protection nature to form in the Cu alloy surface does not move.

[0021]The formation method of nitriding copper on the surface of copper interconnect by this invention is shown in drawing 4. On the silicon wafer 4 in which the silica dioxide 3 was formed, the copper interconnect 1 is formed of dry etching according to the pattern of the photoresist 7 via the metal barrier 6 for preventing diffusion with the metal 5 for taking ohmic contact and copper, and silicon (a). Usually, it oxidizes and oxygen plasma removes a photoresist. However, since copper has exposed the wiring side at this time, copper will also oxidize simultaneously and the reliability of wiring falls remarkably.

[0022]Then, the nitriding copper (Cu-N) 21 is formed in the wiring side by introducing nitrogen gas in the reaction vessel under decompression, making microwave generate nitrogen plasma, and making this nitrogen plasma and copper react selectively (b). Since the nitriding copper 21 formed here is excellent in oxidation resistance, the copper interconnect exposed also in the process (c) which carbonizes a photoresist by next oxygen plasma and is removed does not oxidize. After removing a photoresist, the nitriding copper 22 is formed in the wiring upper part by making it react to the upper part of the wiring which copper exposed, and nitrogen plasma selectively (d).

[0023]Since the surface of the copper interconnect 1 is covered with the above process with the nitriding copper 21 and 22 which is excellent in oxidation resistance, the corrosion of the copper interconnect in a subsequent process is controlled. Since the thickness of the formed nitriding copper is 2-3 nm, an electrical property or the thermal characteristic is not affected. Oxidation of copper in the process of carrying out pattern NINGU of the wiring by this example, and a subsequent process is controlled, and a means to form the wiring excellent in oxidation resistance can be provided.

[0024]The formation method of the compound of copper on the surface of copper interconnect which is other working example of this invention is shown in drawing 5. On the silicon wafer 4 in which the silica dioxide 3 was formed, the copper interconnect 1 is formed via the metal barrier 6 for preventing diffusion with the metal 5 for taking ohmic contact and copper, and silicon (a). The copper-nickel alloy 23 is made to deposit by a sputtering technique all over the silicon wafer top in which this wiring is formed (b). And wiring is formed by etching by chlorine-ammonia nitrogen system gas after circuit pattern depiction (c) by the photoresist 7 (d). Thereby, since copper interconnect is covered with the copper-nickel alloy 23 which is excellent in corrosion resistance, copper interconnect is not corroded in a subsequent process. Corrosion resistance is excellent by this example, and the method of forming the compound which has the same electrical conductivity as copper, heat resistance, and electromigration-proof nature can be provided.

[0025]The formation method of the compound of copper on the surface of copper interconnect by this invention is shown in drawing 6. On the silicon wafer 4 in which the silica dioxide 3 was formed, the ****** copper interconnect 1 is formed in the metal barrier 6 for preventing diffusion with the metal 5 for taking ohmic contact and copper, and silicon (a). The copper-silver alloy 24 is formed with a CVD method (chemical vapor deposition) on this copper interconnect (b). Since the copper-silver alloy 24 formed here is excellent in oxidation resistance, copper interconnect does not oxidize in a subsequent process. Since the thickness of the formed copper-silver alloy is 2-3 nm, an electrical property or the thermal characteristic is not affected. Oxidation resistance is excellent by this example, and the method of forming the compound which has the same electrical conductivity as copper, heat resistance, and electromigration-proof nature can be provided.

[0026]
[Effect of the Invention]In this invention, oxidation of copper interconnect or corrosion is controlled and the outstanding electrical property and thermal characteristic which copper moreover has can be maintained. Therefore, a semiconductor device with high reliability which has the copper interconnect which was excellent in oxidation resistance or a corrosion-resistant pan at electrical conductivity, heat resistance, and electromigration-proof nature can be provided.

[Translation done.]